TABLE V

*p*M *versus* *p*H DATA

$(M^{+2}) = 1 \times 10^{-2}\ M \quad (DTPA) = 2 \times 10^{-2}\ M$

*p*H	Ca^{+2}	Mg^{+2}	Sr^{+2}	Ba^{+2}	Cu^{+2}	Ni^{+2}	Co^{+2}	Zn^{+2}	Cd^{+2}	Fe^{+2}	Mn^{+}
3.0	2.00	2.00	2.00	2.00	8.29	8.26	6.32	6.09	5.52	4.30	2.40
4.0	2.09	2.03	2.00	2.00	10.28	10.20	8.31	8.04	7.68	6.25	4.09
5.0	2.71	2.33	2.11	2.01	12.01	11.68	10.04	9.53	9.76	7.84	5.86
6.0	3.83	3.09	2.82	2.23	13.90	13.19	11.91	11.12	11.78	9.57	7.99
7.0	5.52	4.23	4.54	3.31	15.87	15.07	13.89	13.02	13.77	11.51	9.97
8.0	7.39	5.83	6.43	5.38	17.78	16.97	15.80	14.92	15.69	13.42	11.89
9.0	8.93	7.33	7.98	6.92	19.33	18.51	17.34	16.46	17.23	14.96	13.43
10.0	9.96	8.36	9.01	7.96	20.36	19.54	18.37	17.50	18.26	15.99	14.46
11.0	10.50	8.90	9.55	8.50	20.90	20.08	18.91	18.03	18.80	16.53	15.00
12.0	10.62	9.01	9.66	8.62	21.01	20.20	19.03	18.15	18.92	16.65	15.12
13.0	10.63	9.03	9.68	8.63	21.03	20.21	19.04	18.16	18.93	16.66	15.13
14.0	10.63	9.03	9.68	8.63	21.03	20.21	19.04	18.17	18.93	16.66	15.13

parable data for EDTA.[15] It is immediately evident that DTPA is a more effective chelating than EDTA at high *p*H values due to the greater stability of the MY^{-3} chelate. However, at lower *p*H values, due to the influence of the less stable hydrogen chelate, DTPA is in some cases less effective, *e.g.*, in the Ca^{+2} and Mg^{+2} systems.

Chelates of the type M_2Y^- are not formed to any extent since it has been shown that $pK^{\mathrm{H}}_{\mathrm{MY}}$ is independent of the concentration of metal ion.

If ligand–metal binding in the hydrogen chelates involved only one terminal iminodiacetic acid group the stability would be of the same order of magnitude as the chelates of iminodiacetic acid or methyliminodiacetic acid. However, the chelates are very much more stable indicating a greater degree of ring formation. Several possibilities also exist for the binding in the MY^{-3} chelates; however, no definite choice can be made as to the actual structures from these data alone.

Acknowledgment.—The authors wish to express thanks to the Geigy Chemical Corporation for financial support of this work.

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(15) S. Chaberek, Jr., *Arch. Biochem. Biophys.*, **55**, 322 (1955).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OSAKA UNIVERSITY AND THE OSAKA MUNICIPAL TECHNICAL RESEARCH INSTITUTE]

Infrared Spectra of Metallic Complexes. V. The Infrared Spectra of Nitro and Nitrito Complexes[1]

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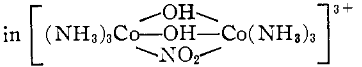
The infrared spectra of nitro and nitrito complexes have been measured in the 5000 ~ 400 cm.$^{-1}$ region. The normal coördinate treatment of the $[Pt(NO_2)_4]^{2-}$ ion has been carried out to give complete assignments. The following conclusions have been obtained: (1) in a series of nitro complexes of various central metals, the metal–nitrogen bond becomes stronger progressively in the order of $[Ni(NO_2)_6]^{4-} < [Co(NO_2)_6]^{3-} < [Pt(NO_2)_4]^{2-}$; (2) the spectra of nitroammine complexes can be correlated with the structure more easily in the KBr region than in the NaCl region; (3) the structure of the nitro bridge in  $\left[(NH_3)_3Co\begin{matrix}-OH-\\-OH-\\-NO_2-\end{matrix}Co(NH_3)_3\right]^{3+}$ ion can be determined by the infrared study; (4) $[Cr(NH_3)_5NO_2]^{2+}$ is spectroscopically shown to be a nitrito and not a nitro complex.

Introduction

Recently Beattie and Tyrrell[3] studied the infrared spectra of a series of nitroammine complexes, $[Co(NH_3)_{6-n}(NO_2)_n]^{(3-n)+}$ in the 5000~650 cm.$^{-1}$ region, and attempted to correlate the stereoisomerism and the number of nitro groups with the infrared spectra. It was found, however, that the spectra were too complicated to allow band assignment because the absorptions due to nitro and ammine groups overlap each other. Faust and Quagliano[4] also compared the infrared spectra of *trans*- and *cis*-$[Co(NH_3)_4(NO_2)_2]Cl$. However, no substantial difference was observed between these two isomers, although the latter exhibits a more complicated spectrum than the former in the 7~8μ region.

It is expected that a study of the infrared spectra of these nitroammine complexes below 650 cm.$^{-1}$ will afford more information, since the Co–NH_3 and Co–NO_2 stretching modes as well as the wagging, rocking and twisting modes of the nitro group appear in this region, and the overlapping of the nitro and ammine bands may possibly be avoided.

The infrared spectra of ammine complexes have already been studied extensively by Powell and Sheppard,[5] and Mizushima, *et al.*[6] In order to

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(2) (a) Department of Chemistry, Clark University, Worcester 10, Massachusetts; (b) Osaka Municipal Technical Research Institute, Osaka, Japan.

(3) I. R. Beattie and H. J. V. Tyrrell, *J. Chem. Soc.*, 2849 (1956).

(4) J. P. Faust and J. V. Quagliano, THIS JOURNAL, **76**, 5346 (1954).

(5) D. B. Powell and N. Sheppard, *J. Chem. Soc.*, 4495 (1956).

(6) S. Mizushima, I. Nakagawa and D. M. Sweeny, *J. Chem. Phys.*, **25**, 1006 (1956).

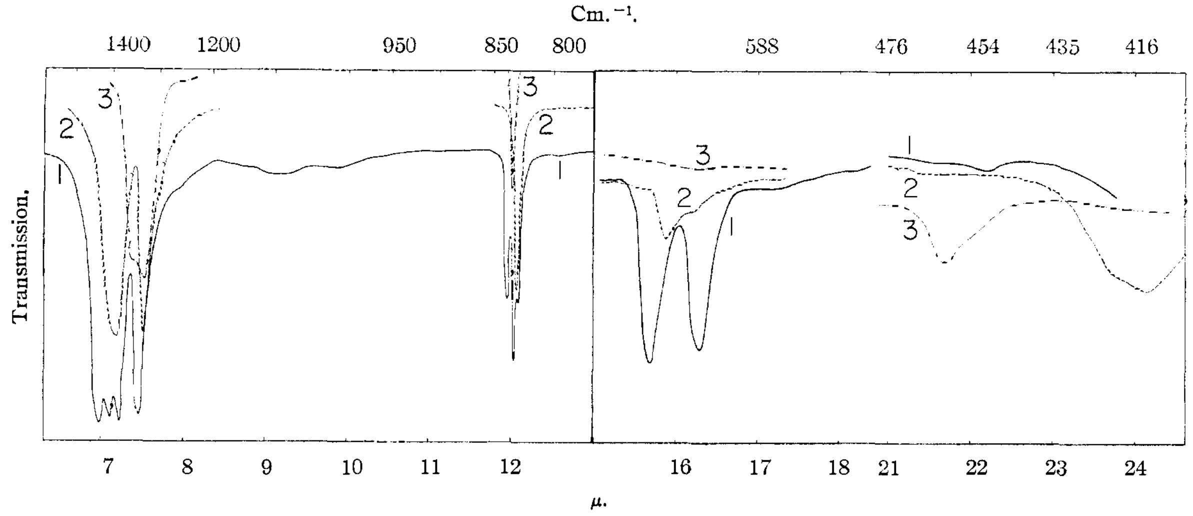
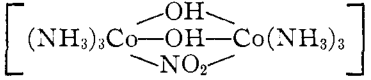


Fig. 1.—Infrared absorption spectra of: (1) ———, $[Pt(NO_2)_4]^{2-}$; - - - -, (2) $[Co(NO_2)_6]^{3-}$; -·-·-·-, (3) $[Ni(NO_2)_6]^{4-}$.

discuss the spectra of nitroammine complexes, it is necessary, therefore, to study the infrared spectra of nitro complexes and to give complete assignments based on the normal coördinate treatment.

In the present paper, the assignments of the infrared spectrum of $[Pt(NO_2)_4]^{2-}$ ion will be made based on the result of the normal coördinate treatment. Combining these results with those of the amine complexes, the spectra of nitroammine complexes will be discussed. In connection with the nitro complexes, the infrared spectra of $[Cr(NH_3)_5NO_2]Cl_2$ and  $\left[(NH_3)_3Co\overset{OH}{\underset{NO_2}{\text{—OH—}}}Co(NH_3)_3\right]Cl_3$ will be studied to determine the structure of the NO_2 group in these complex ions.

indicate the infrared spectra of three nitro complexes in the 5000~400 cm.⁻¹ region. In order to give complete assignments, the normal coördinate treatment was carried out using $[Pt(NO_2)_4]^{2-}$ ion as an example. The detailed method of calculation is given in the Appendix. As is shown in Table II, the agreement between the calculated and observed values is fairly good.

According to the results of the calculation, the bands at 1440~1350 cm.⁻¹ and 838~828 cm.⁻¹ are assigned, respectively, to the stretching and bending vibrations of the nitro group. The Pt–N stretching bands which are most interesting chemically appear weakly near 450 cm.⁻¹ in the infrared and at 319 and 307 cm.⁻¹ in the Raman spectrum. The assumed force constant for this mode is 3.4 × 10^5 dyne/cm. which is nearly equal to 3.43 × 10^5 dyne/cm. obtained for the Pt—C≡N bond in $K_2[Pt(CN)_4]$.[9] Since this value is comparable to the force constants of the C–H and C–C stretching modes in organic molecules, it is concluded that the Pt–NO_2 bond is fairly covalent.

TABLE I

INFRARED SPECTRA OF NITRO COMPLEXES (CM.⁻¹)

Compound	Asym. N–O str.	Sym. N–O str.	NO_2 bend.	NO_2 wagg.	M–N str.
ONO^- ion[a]	1335	1250	830	...	..
$K_2Ca[Ni(NO_2)_6]$[b]	1355	1325	833	462	
$K_3[Co(NO_2)_6]$[c]	1396, 1381	1332	834	630	413
$K_2[Pt(NO_2)_4]$[d]	1436, 1410, 1386	1350	838, 832, 828	636, 613	450
CH_3NO_2[e]	1582	1384	647	599, 476	..

[a] F. A. Miller and C. H. Wilkins, *Anal. Chem.*, **24**, 1253 (1952). [b] A. Rosenheim and I. Koppel, *Z. anorg. Chem.*, **17**, 35 (1898). [c] E. Billmann, *Z. anal. Chem.*, **39**, 284 (1900). [d] M. Vezes, *Bull. soc. chim. France*, **19**, 875 (1898). [e] T. P. Wilson, *J. Chem. Phys.*, **11**, 361 (1943). Only the nitro frequencies are listed in the above table.

Experimental

Preparation.—The compounds used in this investigation were prepared by the usual methods according to the literature given in each table. The purity of each compound was checked by the measurement of the ultraviolet spectrum.[7,8]

Absorption Measurements.—The infrared spectra were obtained by a Perkin-Elmer Model 21 double beam infrared spectrophotometer using NaCl and KBr prisms. The KBr disk method and the Nujol mull technique were employed to obtain the spectra of the NaCl and KBr regions, respectively. The Raman spectrum of a concentrated aqueous solution of $K_2[Pt(NO_2)_4]$ was obtained by a "Yukigosei" Raman spectrograph.

Results and Discussion

I. Nitro Complexes.

—Figure 1 and Table I

As is discussed later, all the nitro complexes exhibit several sharp bands of medium intensity between 630 and 560 cm.⁻¹. Since, in our calculation, the wagging and twisting vibrations of the nitro group are not included, the observed bands near 600 cm.⁻¹ may be the wagging modes of the nitro group which usually have higher frequencies than the twisting modes. Further evidence to support this assignment is seen in nitrito and poly-

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(7) Y. Shimura and R. Tsuchida, *Bull. Chem. Soc. Japan*, **29**, 311 (1956).

(8) S. Yamada, THIS JOURNAL, **73**, 1182 (1951).

(9) D. M. Sweeny, I. Nakagawa, S. Mizushima and J. V. Quagliano, *ibid.*, **78**, 889 (1956).

TABLE II

CALCULATED AND OBSERVED FREQUENCIES OF THE FUNDAMENTALS IN THE $[Pt(NO_2)_4]^{2-}$ ION (CM.$^{-1}$)

Symmetry species	Vibrational modes	Calcd.[c]	Obsd. Infrared	Obsd. Raman[b]
A_{1g}	N–O str.	1347	Inactive	1360
	Pt–N str.	307	Inactive	319
	NO_2 bend.	847	Inactive	842
A_{1u}	NO_2 twist.[a]	. .	Inactive	Inactive
A_{2g}	NO_2 wagg.[a]	. .	Inactive	Inactive
A_{2u}	N–O str.	1445	1440	Inactive
	N–Pt–N bend.[a]	. .	. .	Inactive
	NO_2 rock.	177	?	Inactive
B_{1g}	N–O str.	1338	Inactive	1325
	Pt–N str.	295	Inactive	307
	NO_2 bend.	832	Inactive	835
B_{1u}	NO_2 twist.[a]	. .	Inactive	Inactive
B_{2g}	N–Pt–N bend.	269	Inactive	245
	NO_2 wagg.[a]	. .	Inactive	?
B_{2u}	N–O str.	1445	Inactive	Inactive
	N–Pt–N bend.[a]	. .	Inactive	Inactive
	NO_2 rock.	177	Inactive	Inactive
E_g	N–O str.	1444	Inactive	1410
	NO_2 rock.	183	Inactive	185
	NO_2 twist.[a]	. .	Inactive	?
E_u	N–O str.	1313	1335	Inactive
	Pt–N str.	428	450	Inactive
	NO_2 bend.	867	833	Inactive
	N–Pt–N bend.	200	?	Inactive
	NO_2 wagg.[a]	. .	636, 613	Inactive

[a] Out-of-plane modes. [b] The reported Raman lines of $Na_2[Pt(NO_2)_4]$ are 307, 321(p), 835, 847(p), 1325, 1364, 1412. Here (p) denotes polarized line. (Mathieu and Cornevin, *J. chim. phys.*, **36**, 271 and 308 (1939)). [c] The Pt–N and N–O distances were taken as 2.02 and 1.22 Å., respectively, according to the result of X-ray analysis. Furthermore, these angles were assumed: $\alpha = \alpha' = \beta = 120°$, $\delta = 90°$ (see Appendix).

nuclear nitro bridge complexes which show no such bands near 600 cm.$^{-1}$.

Table I also compares the spectra of nitro complexes with those of CH_3NO_2 (the C–N bond is covalent) and free ONO^- ion. It is interesting to note that the asymmetric nitro stretching frequency increases progressively in the order of ONO^- ion $< [Ni(NO_2)_6]^{4-} < [Co(NO_2)_6]^{3-} < [Pt(NO_2)_4]^{2-} <$ CH_3NO_2. As already pointed out by Beattie and Tyrrell,[3] the separation between the asymmetric and symmetric nitro stretching frequencies increases as the metal–nitrogen bond becomes stronger. The symmetric stretching mode does not show a large shift as in the case of organic nitro compounds.[10] Therefore the above result seems to indicate that the metal–nitrogen bond becomes stronger in the order of Ni<Co<Pt.

The nitro bending mode at *ca.* 830 cm.$^{-1}$ does not move appreciably. However, the wagging vibration near 600 cm.$^{-1}$ shows a shift in each compound. It already has been found[11] that the wagging, rocking and twisting modes of the ligand are shifted to higher frequencies as the metal–ligand bond becomes stronger. Therefore, the low frequency of the wagging mode in the Ni-complex may indicate the weakness of the Ni–N bond. The observation that the metal–nitrogen stretching frequency is higher in the Pt- than in the Co-complex suggests that the bond is stronger in the former than in the latter. All of the above mentioned facts lead to the conclusion that the metal–nitrogen bond becomes stronger in the order of Ni < Co < Pt.

II. Nitroammine Complexes.—As stated before, the complexity of the spectra of nitroammine complexes in the NaCl region makes it difficult to discuss the relation between the spectra and the structure of the complexes. In the KBr region, however, no overlapping of the nitro and ammine bands is observed, since the nitro wagging vibrations usually are located near 600 cm.$^{-1}$ whereas the $Co–NH_3$ stretching bands are around 500 cm.$^{-1}$.[5] Figure 2a and 2b show the spectra of the nitroammine complexes in the nitro wagging and the $Co–NH_3$ stretching regions, respectively.

Table III indicates that the number of the nitro wagging bands depends on the symmetry of the complex ion. For example, 1,2-$[Co(NH_3)_4(NO_2)_2]^+$ has two bands at 605 and 587 cm.$^{-1}$, whereas 1,6-$[Co(NH_3)_4(NO_2)_2]^+$ shows only one band at 623

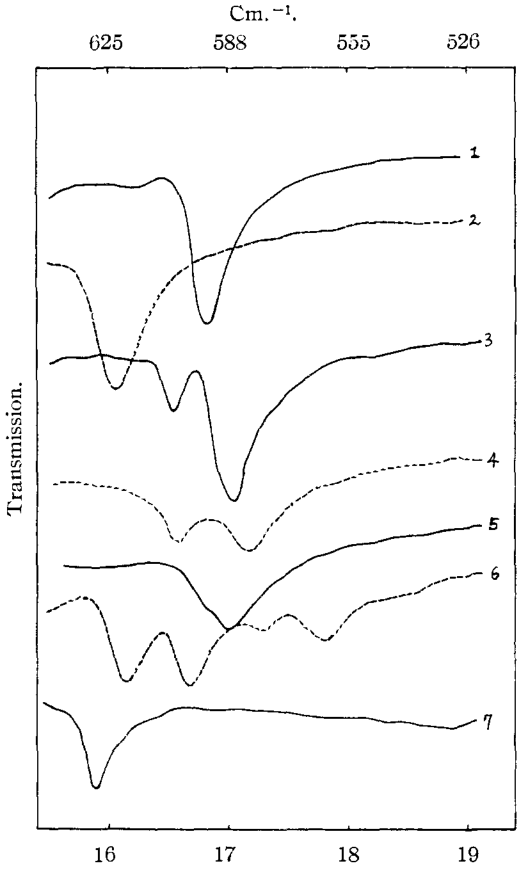

Fig. 2a.—Infrared absorption spectra of nitroammine Co(III) complexes in the 630 ~ 525 cm.$^{-1}$ region: (1) $[Co(NH_3)_5(NO_2)]^{2+}$; (2) 1,6-$[Co(NH_3)_4(NO_2)_2]^+$; (3) 1,2-$[Co(NH_3)_4(NO_2)_2]^+$; (4) 1,2,4-$[Co(NH_3)_3(NO_2)_3]$; (5) 1,2,3-$[Co(NH_3)_3(NO_2)_3]$; (6) 1,6-$[Co(NH_3)_2(NO_2)_4]^-$; (7) $[Co(NO_2)_6]^{3-}$.

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(10) J. F. Brown, Jr., THIS JOURNAL, **77**, 6341 (1955).

(11) J. Fujita, K. Nakamoto and M. Kobayashi, *ibid.*, **78**, 3295 (1956).

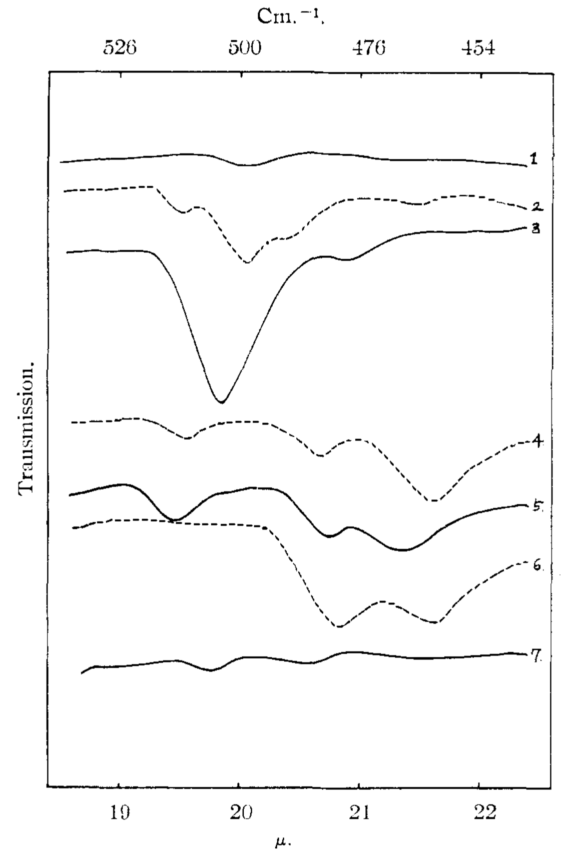

Fig. 2b.—Infrared absorption spectra of nitroammine Co(III) complexes in the 525 ~ 450 cm.$^{-1}$ region: (1) $[Co(NH_3)_6]^{3+}$; (2) $[Co(NH_3)_5(NO_2)]^{2+}$; (3) 1,6-$[Co(NH_3)_4(NO_2)_2]^+$; (4) 1,2-$[Co(NH_3)_4(NO_2)_2]^+$; (5) 1,2,4-$[Co(NH_3)_3(NO_2)_3]$; (6) 1,2,3-$[Co(NH_3)_3(NO_2)_3]$; (7) 1,6-$[Co(NH_3)_2(NO_2)_4]^-$.

cm.$^{-1}$. The two isomers of $[Co(NH_3)_3(NO_2)_3]$ also exhibit the wagging bands of different numbers.

TABLE III

INFRARED SPECTRA OF Co(III) NITROAMMINE COMPLEXES IN THE KBr REGION (CM.$^{-1}$)

Compound	Prep.	NO_2 wagg.	Co–NH_3 str
$[Co(NH_3)_6]^{3+}$	*a*	...	502
$[Co(NH_3)_5NO_2]^{2+}$	*b*	594	513, 499, 488
1,6-$[Co(NH_3)_4(NO_2)_2]^+$	*c*	623	504
1,2-$[Co(NH_3)_4(NO_2)_2]^+$	*d*	605, 587	511 484, 463
1,2,4-$[Co(NH_3)^3(NO_2)_3]$	*e*	603, 582	514, 483, 469
1,2,3-$[Co(NH_3)_3(NO_2)_3]$	*f*	588	481, 464
1,6-$[Co(NH_3)_2(NO_2)_4]$	*g*	619, 600, 578, 563	507, 488
$[Co(NO_2)_6]^{3-}$	*h*	630	....

[a] "Inorganic Syntheses," Vol. II, p. 217, 1946. [b] W. D. Harkins, R. E. Hall and W. A. Roberts, THIS JOURNAL, **38**, 2646 (1916). [c] S. M. Jorgensen, *Z. anorg. Chem.*, **17**, 473 (1898). [d] S. M. Jorgensen, *ibid.*, **17**, 469 (1898). [e] S. M. Jorgensen, *ibid.*, 17, 475 (1898). [f] M. Shibata, presented before the symposium on metallic complexes, Nagoya, Japan, November, 1957. Dr. Shibata kindly provided the compound for us. [g] S. M. Jorgensen, *Z. anorg. Chem.*, **17**, 477 (1898). [h] E. Billmann, *Z. anal. Chem.*, **39**, 284 (1900).

The Co–NH_3 stretching bands are concentrated near 500 cm.$^{-1}$. If we assume O_h symmetry[12] for $[Co(NH_3)_6]^{3+}$ ion, the Co–NH_2 stretching modes belong to the triply degenerate F_{1u} species. Therefore, substitution of NH_3 by NO_2^- will lower the symmetry and split this mode. Table IV compares the number of the observed Co–NH_3 stretching modes with the number predicted by the correlation table. The fair agreement between the calculated and the observed numbers of these modes seems to support the band assignment. The detailed discussion on the metal–ammine stretching bands will be given in the following paper of this series.

TABLE IV

COMPARISON OF THE PREDICTED AND THE OBSERVED NUMBERS OF THE Co–NH_3 STRETCHING BANDS IN NITROAMMINE COMPLEXES

Compound	Assumed sym.	Species of infrared active bands	No. of predicted bands	No. of obsd. band
$[Co(NH_3)_6]^{3+}$	O_h	F_{1u}	1	1
$[Co(NH_3)_5NO_2]^{2+}$	C_{4v}	$2A_1$, E	3	3
1,6-$[Co(NH_3)_4(NO_2)_2]^+$	D_{4h}	E_u	1	1
1,2-$[Co(NH_3)_4(NO_2)_2]^+$	C_{2v}	$2A_1$, B_1, B_2	4	3
1,2,4-$[Co(NH_3)_3(NO_2)_3]$	C_{2v}	$2A_1$, B_2	3	3
1,2,3-$[Co(NH_3)_3(NO_2)_3]$	C_{3v}	A_1, E	2	2
1,6-$[Co(NH_3)_2(NO_2)_4]^-$	D_{4h}	A_{2u}	1	2

III. Nitrito Complexes.—$[Co(NH_3)_5NO_2]^{2+}$ ion has two isomers; one is a nitro complex linked to the metal through nitrogen, and the other is a nitrito complex linked through an oxygen atom of the nitro group. It is well known that the unstable red form of the nitrito complex rearranges spontaneously to the stable yellow form of the nitro complex either in solution or in the solid state.

The infrared study of the conversion between these two isomers has been made by Penland, *et al.*[13] Beattie and Satchell[14] also have studied the kinetics of this conversion.

It would be interesting to know if the same trend is seen in $[Cr(NH_3)_5NO_2]Cl_2$. Table V compares the spectrum of $[Cr(NH_3)_5NO_2]Cl_2$ with the analogous cobaltic complexes. The result definitely indicates that the Cr(III) complex exists as a nitrito form since its spectrum is almost identical with that of the Co(III) nitrito complex. For Cr(III), the nitrito form is much more stable than the nitro form and, indeed, the nitro complex has not yet been observed. The absence of the characteristic bands of the nitro complex near 600 cm.$^{-1}$ (wagging mode) also suggests that the NO_2 group is linked to the metal through an oxygen atom. This result agrees with that of Linhard, *et al.*,[15] obtained by the study of the ultraviolet spectra.

As is shown in Table VI, all the Cr(III) ammine complexes so far observed exhibit several bands near 450 cm.$^{-1}$. It is anticipated that these bands are due to the Cr–NH_3 stretching modes. A shift to lower frequencies of the Cr–NH_3 stretching relative to the Co–NH_3 stretching modes may indicate that the latter bond is stronger than the former.

The differences between the spectra of the nitro and nitrito complexes are useful in determining the structure of the nitro bridge in the polynuclear

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(12) If only the Co–N_6 skeleton is considered, the point group is expressed by O_h.

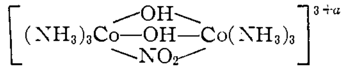
(13) R. B. Penland, T. J. Lane and J. V. Quagliano, THIS JOURNAL, **78**, 887 (1956).

(14) I. R. Beattie and D. P. N. Satchell, *Trans. Faraday Soc.*, **52**, 1590 (1956).

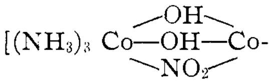
(15) M. Linhard, H. Siebert and M. Weigel, *Z. anorg. Chem.*, **278**, 288 (1955).

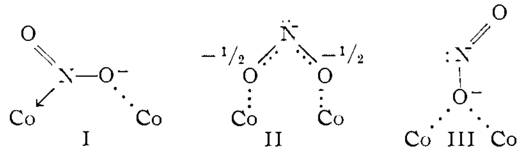
TABLE V

INFRARED SPECTRA OF NITRITO COMPLEXES (CM.$^{-1}$)

Compound	Asym. NO str.	Sym. NO str.	NO_2 bend.	NO_2 wagg.	Co–N str.	Cr–N str.
$[Co(NH_3)_5NO_2]^{2+}$	1428	1310	824	594	499	....
$[Co(NH_3)_5ONO]^{2+}$	1468	1065	825	..	?	....
$[Cr(NH_3)_5ONO]^{2+}$	1460	1048	839	..	..	476, 466, 444
 $\left[(NH_3)_3Co\overset{OH}{\underset{NO_2}{—OH—}}Co(NH_3)_3\right]^{3+a}$	1516	1200	830	..	500	....

[a] A. Werner, A. Grun and E. Bindschedler, *Ann.*, **375**, 123 (1910).

complex. For example, in  $[(NH_3)_3\,Co\overset{OH}{\underset{NO_2}{—OH—}}Co(NH_3)_3]Cl_3$, the following structures are possible



I II III

As is shown in Table V, the NO stretching frequencies of this complex are markedly different from those of nitro and nitrito complexes. This result may rule out the structure III since III is expected to exhibit similar frequencies to that of the nitrito complexes. Structure II also has a difficulty to explain the high asymmetric stretching frequency of this complex. Therefore, the structure I which has one Co–N and one Co–O bond is most probable from the infrared study.

TABLE VI

THE Cr(III)-NH_3 STRETCHING FREQUENCIES IN VARIOUS AMMINE COMPLEXES

Compound	Cr-NH_3 str. band (cm.$^{-1}$)
$[Cr(NH_3)_6]^{3+}$	455 (broad, weak)
$[Cr(NH_3)_5Cl]^{2+}$	470, 460, 431
$[Cr(NH_3)_5ONO]^{2+}$	476, 466, 444
$[Cr(NH_3)_5N_3]^{2+}$	448

TABLE VII

CLASSIFICATION OF THE NORMAL VIBRATIONS BELONGING TO EACH CLASS OF SYMMETRY

		In-plane modes					Out-of-plane modes			
Class	No. of vib.	NO str.	Pt–N str.	NO_2 bend.	Pt–N bend.	NO_2 rock.	NO_2 wagg.	NO_2 twist.	Pt–N bend.	Activity
A_{1g}	3	1	1	1	0	0	0	0	0	Raman
A_{1u}	1	0	0	0	0	0	0	1	0	Inactive
A_{2g}	1	0	0	0	0	0	1	0	0	Inactive
A_{2u}	3	1	0	0	0	1	0	0	1	Infrared
B_{1g}	3	1	1	1	0	0	0	0	0	Raman
B_{1u}	1	0	0	0	0	0	0	1	0	Inactive
B_{2g}	2	0	0	0	1	0	1	0	0	Raman
B_{2u}	3	1	0	0	0	1	0	0	1	Inactive
E_g	3	1	0	0	0	1	0	1	0	Raman
E_u	5	1	1	1	1	0	1	0	0	Infrared

Appendix

The following procedure was used in the calculation of the normal vibrations of the $[Pt(NO_2)_4]^{2-}$ ion. According to the X-ray analysis of Lambot[16] the platinum and the four nitrogen atoms form a square plane, each O–N–O plane being tilted 69°50′ to the square plane. However, it is desirable to assume a model of higher symmetry to reduce the order of the secular equation. It is evident that a complete planar structure including the oxygens is not probable because of the close approach of the two oxygens of the neighboring nitro groups. Therefore, a structure such as shown in Fig. 3 was assumed in which all the four nitro planes are perpendicular to the Pt–N square plane.[17]

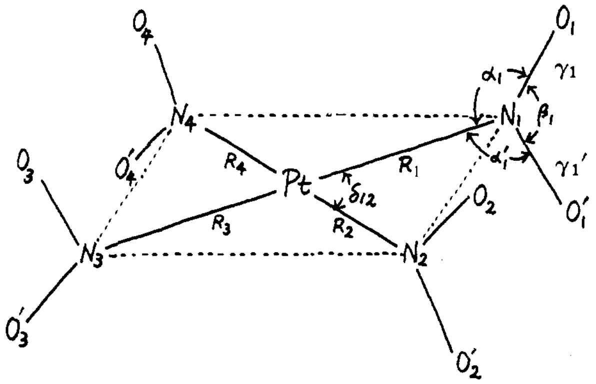


Fig. 3.—Assumed model of $[Pt(NO_2)_4]^{2-}$ ion.

The point group of this model is D_{4h}. Then, the thirty-three normal vibrations are grouped into ten classes as shown in Table VII. Among those, twenty-three are in-plane vibrations which are calculated in this paper. The remaining ten vibrations are out-of-plane and separable from the in-plane vibrations.[18]

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[16] H. Lambot, *Bull. Sci. Liege*, **12**, 463, 541 (1943).

[17] Since such a model is different from the actual configuration, the force constants obtained (Table X) may not be accurate. Nevertheless, this assumption was made because the main purpose of calculation is to give band assignments, and not to determine an accurate set of the force constants.

[18] It is generally shown that the interaction between the in-plane and the out-of-plane modes is fairly small when the Urey–Bradley field is used to express the potential energy. (See, S. Mizushima, "Structure of Molecules and Internal Rotation," Academic Press, New York, N. Y., 1954, p. 215.) In the present case, all the off-diagonal terms of the *F*-matrices and the *G*-matrices which represent the interaction between these two modes vanish, except the one with the N–Pt–N bending in the E_u which is, however, estimated to be fairly small.

TABLE VIII

THE SYMMETRY COÖRDINATES FOR THE IN-PLANE VIBRATIONS

A_{1g} $S_1 = 1/\sqrt{8}[(r_1 + r_1') + (r_2 + r_2') + (r_3 + r_3') + (r_4 + r_4')]$
$S_2 = 1/2[R_1 + R_2 + R_3 + R_4]$
$S_3 = 1/\sqrt{24}[2\beta_1 + 2\beta_2 + 2\beta_3 + 2\beta_4 - (\alpha_1 + \alpha_1') - (\alpha_2 + \alpha_2') - (\alpha_3 + \alpha_3') - (\alpha_4 + \alpha_4')]$
A_{2u} $S_4 = 1/\sqrt{8}[(r_1 - r_1') + (r_2 - r_2') + (r_3 - r_3') + (r_4 - r_4')]$
$S_5 = 1/\sqrt{8}[(\alpha_1 - \alpha_1') + (\alpha_2 - \alpha_2') + (\alpha_3 - \alpha_3') + (\alpha_4 - \alpha_4')]$
B_{1g} $S_6 = 1/\sqrt{8}[(r_1 + r_1') - (r_2 + r_2') + (r_3 + r_3') - (r_4 + r_4')]$
$S_7 = 1/2[R_1 - R_2 + R_3 - R_4]$
$S_8 = 1/\sqrt{24}[2\beta_1 - 2\beta_2 + 2\beta_3 - 2\beta_4 - (\alpha_1 + \alpha_1') + (\alpha_2 + \alpha_2') - (\alpha_3 + \alpha_3') + (\alpha_4 + \alpha_4')]$
B_{2g} $S_9 = 1/2[\delta_{12} - \delta_{23} + \delta_{34} - \delta_{41}]$
B_{2u} $S_{10} = 1/\sqrt{8}[(r_1 - r_1') - (r_2 - r_2') + (r_3 - r_3') - (r_4 - r_4')]$
$S_{11} = 1/\sqrt{8}[(\alpha_1 - \alpha_1') - (\alpha_2 - \alpha_2') + (\alpha_3 - \alpha_3') - (\alpha_4 - \alpha_4')]$
E_g[a] $S_{12} = 1/\sqrt{8}[(r_1 - r_1') + (r_2 - r_2') - (r_3 - r_3') - (r_4 - r_4')]$
$S_{13} = 1/\sqrt{8}[(\alpha_1 - \alpha_1') + (\alpha_2 - \alpha_2') - (\alpha_3 - \alpha_3') - (\alpha_4 - \alpha_4')]$
E_u[a] $S_{14} = 1/\sqrt{8}[(r_1 + r_1') + (r_2 + r_2') - (r_3 + r_3') - (r_4 + r_4')]$
$S_{15} = 1/2[R_1 + R_2 - R_3 - R_4]$
$S_{16} = 1/\sqrt{24}[2\beta_1 + 2\beta_2 - 2\beta_3 - 2\beta_4 - (\alpha_1 + \alpha_1') - (\alpha_2 + \alpha_2') + (\alpha_3 + \alpha_3') + (\alpha_4 + \alpha_4')]$
$S_{17} = 1/2[\delta_{12} + \delta_{23} - \delta_{34} - \delta_{41}]$

[a] For the doubly degenerate vibrations, only one coördinate is given for each pair.

TABLE IX

THE G AND F-MATRICES OF THE $[Pt(NO_2)_4]^{2-}$ ION

Here, R = (Pt–N) distance $\tau = 1/R$
r = (N–O) distance $\tau' = 1/r$

$$s = \frac{1}{R^2 + r^2 + Rr}$$

μ_N, μ_{Pt}, and μ_O are reciprocal masses of N, Pt and O atoms, respectively.
K, K_1, H, H_1, H_O, F, F_O and F_1 are the force constants (see Table X).

G-matrices

A_{1g}, B_{1g}
$G_{11} = \mu_N$ $G_{22} = \frac{1}{2}\mu_N + \mu_O$
$G_{12} = -\frac{\sqrt{2}}{2}\mu_N$ $G_{23} = -\frac{3}{2}\tau'\mu_N$
$G_{13} = \frac{\sqrt{3}}{2}\sqrt{2}\tau'\mu_N$ $G_{33} = 3\tau'^2\mu_O + \frac{9}{2}\tau'^2\mu_N$

A_{2u}, B_{2u}
$G_{11} = \frac{3}{2}\mu_N + \mu_O$
$G_{12} = -\frac{\sqrt{3}}{2}\mu_N(2\tau + \tau')$
$G_{22} = \tau'^2\mu_O + \mu_N\left(2\tau^2 + 2\tau\tau' + \frac{1}{2}\tau'^2\right)$

B_{2g}
$G_{11} = 4\tau^2\mu_N$

E_g
$G_{11} = \frac{3}{2}\mu_N + \mu_O$
$G_{12} = -\frac{\sqrt{3}}{2}\mu_N(2\tau + \tau')$
$G_{22} = 4\tau^2\mu_{Pt} + \tau'^2\mu_O + \left(2\tau^2 + 2\tau\tau' + \frac{1}{2}\tau'^2\right)\mu_N$

E_u
$G_{11} = \frac{1}{2}\mu_N + \mu_O$ $G_{22} = 2\mu_{Pt} + \mu_N$
$G_{12} = -\frac{\sqrt{2}}{2}\mu_N$ $G_{23} = \frac{3}{2}\sqrt{2}\tau'\mu_N$
$G_{13} = -\frac{3}{2}\tau'\mu_N$ $G_{24} = -2\tau\mu_{Pt}$
$G_{33} = 3\tau'^2\mu_O + \frac{9}{2}\tau'^2\mu_N$
$G_{14} = G_{34} = 0$ $G_{44} = 2\tau^2(2\mu_{Pt} + \mu_N)$

F-matrices

A_{1g}
$$F_{11} = K_1 + \frac{3}{2}F + \frac{1}{4}F_1s\left(4r^2 + 4Rr + \frac{7}{10}R^2\right)$$
$$F_{12} = \frac{\sqrt{2}}{4}F_1s\left(2R^2 + 2r^2 + \frac{53}{10}Rr\right)$$
$$F_{13} = \frac{9}{20}Fr - \frac{1}{4}F_1Rs\left(2r^2 + \frac{9}{10}Rr - \frac{1}{5}R^2\right)$$

TABLE IX (*continued*)

$$F_{22} = K + 2F_O + \frac{1}{4}F_1s\left(4R^2 + 4Rr + \frac{7}{10}r^2\right)$$

$$F_{23} = -\frac{1}{2\sqrt{2}}F_1rs\left(2R^2 + \frac{9}{10}Rr - \frac{1}{5}r^2\right)$$

$$F_{33} = \frac{2}{3}\left(H + \frac{13}{40}F\right)r^2 + H_1 + \frac{1}{20}F_1s\left(R^2 + r^2 + \frac{35}{2}Rr\right)$$

A_{2u}, B_{2u}, E

$$F_{11} = K_1 - \frac{1}{20}F + \frac{1}{2}F_1s\left(4R^2 + 4Rr + \frac{7}{10}r^2\right)$$

$$F_{12} = \frac{\sqrt{3}}{4}Rs\left[F_1r(2r + R) - \frac{1}{10}F_1R(2R + r)\right]$$

$$F_{22} = H_1Rr + \frac{1}{4}Rrs\left[3F_1Rr + \frac{1}{10}F_1(2R + r)(2r + R)\right]$$

B_{1g}

$$F_{11} = F_{11}{}^{A_{1g}}$$

$$F_{12} = F_{12}{}^{A_{1g}}$$

$$F_{22} = K - \frac{1}{5}F_O + \frac{1}{2}F_1s\left(4R^2 + 4rR + \frac{7}{10}r^2\right)$$

B_{2g}

$$F_{11} = \left(H_O + \frac{11}{20}F_O\right)R^2$$

E_u

$$F_{11} = K_1 + \frac{3}{2}F + \frac{1}{4}F_1s\left(4r^2 + 4Rr + \frac{7}{10}R^2\right)$$

$$F_{12} = F_{12}{}^{A_{1g}} \qquad F_{13} = F_{13}{}^{A_{1g}}$$

$$F_{14} = F_{34} = O$$

$$F_{22} = K + \frac{9}{10}F_O + \frac{1}{2}s\left[(2R + r)^2F_1 - \frac{3}{10}r^2F_1\right]$$

$$F_{23} = F_{23}{}^{A_{1g}} \qquad F_{33} = F_{33}{}^{A_{1g}} \qquad F_{24} = \frac{9}{20}F_OR$$

$$F_{44} = \left(H_O + \frac{11}{20}F_O\right)R^2$$

The symmetry coördinates for the in-plane modes are given in Table VIII. Using these symmetry coordinates, the secular equation was set up according to the procedure of Wilson.[19] The *G* and *F*-matrices are calculated as shown in Table IX. An Urey–Bradley type field[20] was used to express the potential energy. The values of the force constants which give the best fit with the observed infrared and Raman frequencies are given in Table X.

TABLE X

FORCE CONSTANTS OF $[Pt(NO_2)_4]^{2-}$ ION (10^5 DYNE/CM.)

Str.	Bend.	Repulsive
K(Pt–N) = 3.40	*H*(O–N–O) = 0.15	*F*(O....O) = 3.0
K_1(N–O) = 7.30	H_1(Pt–N–O) = 0.08	F_0(N....N) = 0.2
	H_0(N–Pt–N) = 0.04	F_1(Pt....O) = 0.03

Using these values of the force constants, the calculations have been made according to the usual procedure,[19] and the results are shown in Table II.

OSAKA, JAPAN

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[19] E. B. Wilson, *J. Chem. Phys.*, **7**, 1047 (1939); **9**, 76 (1941).

[20] T. Shimanouchi, *ibid.*, **17**, 245, 734, 848 (1949).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Proton Resonance Spectra and Structures of Mercury(II)-Olefin Addition Compounds

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The proton resonance spectra of methyl ethyl ether, $CH_3OCH_2CH_2HgOCOCH_3$ and $HOCH_2CH_2HgOH$ are reported. The first two were measured in CCl_4 solution and the measured chemical shifts extrapolated to infinite dilution. The last compound was measured in basic D_2O and shifts again extrapolated to infinite dilution. The results conclusively support the above structures for the mercury compounds on the basis of observed area ratios and spin–spin hyperfine structure. The relative chemical shifts of the several types of methyl and methylene groups are in general accord with expectation from previous studies.

Introduction

As part of a broad study of the nuclear resonance spectra and structures of the addition compounds formed by various metals with alkenes and alkynes, we have investigated the proton resonance spectra of two simple but typical olefin adducts of mercury (II) salts, *viz.*, $CH_3COOHgCH_2CH_2OCH_3$ and $HOCH_2CH_2HgOH$. Aside from its intrinsic interest, this study serves a purpose in our over-all program of providing data on olefin–metal complexes for which there is good evidence that addition of HgX_2 across the double bond to give a carbon–mercury(II) σ-bond has occurred.[1] It is found that, conversely, the proton resonance spec-

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[1] For comprehensive discussion of this point see G. F. Wright, *Ann. N. Y. Acad. Sci.*, **65**, 436 (1957), and J. Chatt, *Chem. Revs.*, **48**, 7 (1951).